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Ultrasonic study of molecular interactions in ternary mixtures of dimethyl sulphoxide (1) + carbon tetrachloride (2) + aromatic hydrocarbons (3) at 308.15 K

A Ali[a], K Tiwari[a], A K Nain[a] and V Chakravortty[b]

[a]Department of Chemistry, Jamia Millia Islamia, New Delhi-110 025, India

[b]Department of Chemistry, Utkal University, Bhubaneswar-751 004, Orissa, India

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Abstract : The ultrasonic velocity and density have been measured for dimethyl sulphoxide (DMSO) + carbon tetrachloride + benzene, + toluene and + chlorobenzene, at 308.15 K. The acoustical parameters such as isentropic compressibility, intermolecular free length, molar volume and acoustic impedance have been obtained for all the mixtures from experimental data with a view to investigating the exact nature of the molecular interaction. The excess values of the said parameters have also been calculated and found to be useful in estimating the strength of the interactions in the mixtures.

Keywords : Ternary liquid mixtures, acoustical parameters, molecular interaction

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1. Introduction

Investigations on binary and ternary mixtures of nonelectrolytes by calculating excess thermodynamic parameters are found to be highly useful in understanding the solute-solvent interactions in these mixtures. Ultrasonic wave propagation affects the physical properties of the medium and hence, can furnish information on the physics of the liquid and liquid mixtures. The measured ultrasonic parameters are being extensively used to study intermolecular processes in liquid systems [1–3]. The sign and magnitude of non-linear deviations from ideal values of velocities and isentropic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules [4]. The present investigation is a continuation of our studies on thermodynamic properties of binary and ternary liquid mixtures containing dimethyl sulphoxide (DMSO). DMSO is a versatile compound, used as a cryoprotectant for macromolecules, organelles, cells and tissues [5]. It is widely used as solvent, plasticizer and chemical intermediates. Binary and ternary mixtures of DMSO with aromatic solvents are of interest in studies of polymer miscibility, polymer phase diagrams and preferential interaction of polymers in mixed solvents [6–8]. Therefore, a better understanding of the physicochemical properties of mixed solvent systems : I-DMSO + carbon tetrachloride + benzene, II-DMSO + carbon tetrachloride + toluene and III-DMSO + carbon tetrachloride + chlorobenzene may help in the study of chemical and biological processes in these media. Moreover, no ultrasonic or volumetric behaviour of these ternary mixtures are reported in the literature.

The present paper deals with the study of ultrasonic velocity u, isentropic compressibility K_s, intermolecular free length L_f, molar volume V, acoustic impedance Z and their excess values for these ternary systems. The results throw light on intermolecular interaction between the component molecules of the mixtures.

2. Experimental

Dimethyl sulphoxide, carbon tetrachloride, benzene, toluene and chlorobenzene used were of analytical grade (E. Merck and BDH). DMSO used was 99.5% pure and was further purified by the methods described by Gopal *et al* [9].

Benzene was purified by the methods described by Naidu and Krishnan [10]. Carbon tetrachloride, toluene and chlorobenzene were purified by standard methods described in the literature [11,12]. The densities of pure liquids and their mixtures were measured using a single-capillary pycnometer (made of Borosil glass) of bulb capacity 8×10^{-3} dm^3. The marks on the capillary were calibrated with triple distilled water. The accuracy in density measurements was found to be ±0.0001 g cm^{-3}. The ultrasonic velocities of pure liquids and their mixtures were measured using single crystal variable path interferometer at 2 MHz by the methods of Subrahmanyam and Murthy [13] with an accuracy of ±0.05%. The temperature of the test liquids and their mixtures was maintained to an accuracy of ±0.02 K in an electronically controlled thermostatic water bath. Nine ternary mixtures of DMSO with carbon tetrachloride and aromatic hydrocarbons were prepared by weight in the increasing mole fraction of DMSO. The purity of the chemicals was checked by comparing the densities and ultrasonic velocities of pure liquids with those reported in the literature [14-16].

3. Results and discussion

The dependence of ultrasonic velocity, u on mole fraction x of DMSO in all the three ternary liquid mixtures was checked by a polynomial equation

$$\ln u(x) = \sum \ln u_i x^i . \tag{1}$$

The coefficients $\ln u_i$ along with the standard deviations $\sigma(\ln u)$ for the ternary mixtures are presented in Table 1. It is found that eq. (1) reproduces the experimental ultrasonic velocities within ±1.0022, ±1.0034 and ±1.0014, respectively, for the three ternary liquid systems under study.

Table 1. Coefficients ($\ln u_i$) of eq (1) along with standard deviations σ ($\ln u$) for the ternary systems

System	$\ln u_0$	$\ln u_1$	$\ln u_2$	$\ln u_3$	$\ln u_4$	$\sigma(\ln u)$
DMSO + CCl_4 + C_6H_6	7 0571	0 1754	0 3634	0 7604	-0 4082	0 0022
DMSO + CCl_4 + $C_6H_5CH_3$	7 0100	0 5390	-1 7911	0 3196	-1 8134	0 0034
DMSO + CCl_4 + C_6H_5Cl	7 0778	-0.0103	0 2091	0 0072	-0 0446	0 0014

From the measured ultrasonic velocity and density ρ, the isentropic compressibility, K_s of a solution is determined by using the relation [17]

$$K_s = 1/\rho u^2 . \tag{2}$$

The ultrasonic velocity is also influenced by the acoustic impedance, Z given by the relation [18]

$$Z = u\rho. \tag{3}$$

The intermolecular free length, L_f is the distance covered by a sound wave between the surfaces of the neighbouring molecules, and is given by Jacobson [19] :

$$L_f = K(K_s)^{1/2}, \tag{4}$$

where K is the temperature-dependent constant. The excess properties have been calculated using the following general equation

$$A^E = A_{\text{mixture}} - (x_1A_1 + x_2A_2 + x_3A_3), \tag{5}$$

where A_1 is the parameter (K_s, L_f, V, Z) for DMSO; A_2 and A_3 are the same parameters for CCl_4 and aromatic hydrocarbons, respectively; x_1, x_2 and x_3 are the mole fractions of DMSO, CCl_4 and aromatic hydrocarbons, respectively, (volume fraction ϕ instead of x is used for calculation of K_s^E).

The experimental values of densities and ultrasonic velocities and calculated values of K_s, L_f, V and Z at 308.15 K over the entire composition range are presented in Table 2. The excess functions K_s^E, L_f^E, V^E and Z^E of all the three ternary systems, evaluated using eq. (5), are summarised in Table 3. It is evident from Table 2 that ultrasonic velocity and acoustic impedance increases while molar volume, isentropic compressibility and intermolecular free length decrease with the increase in concentration of DMSO in all the mixtures. The pronounced increase or decrease in these parameters with composition of the mixtures indicates the presence of interaction between the component molecules in the ternary mixtures. The values of excess isentropic compressibility, K_s^I (Table 3) are almost negative in DMSO + CCl_4 + C_6H_6 system which suggest that structure making effect [20-22] is predominant in this system. This decreases the free spaces between the molecules in the mixtures, due to increased molecular interaction, which would, in turn, provide a negative deviation in compressibility. Table 3 shows that the values of K_s^I for the systems DMSO + CCl_4 + $C_6H_5CH_3$ and DMSO + CCl_4 + C_6H_5Cl are positive upto x_1 ~0.5722 and 0.5658, while they become negative at higher mole fraction of DMSO. A change in sign in K_s^E from positive to negative as the amount of DMSO in these mixtures increases is indicative of increased interaction between the component molecules of the mixtures. Fort and Moore [4] have suggested that K_s^E becomes increasingly negative as the strength of interaction between molecules increases.

In the system DMSO + CCl_4 + C_6H_6, DMSO is highly polar (dipole moment μ = 3.96 D) [23] while both CCl_4 and C_6H_6 are non-polar (μ = 0) [23]. Mixing of benzene/carbon tetrachloride with DMSO tends to break

Table 2. Values of density (ρ), ultrasonic velocity (u), isentropic compressibility (K_s) intermolecular free length (L_f), molar volume (V) and acoustic impedance (Z) of (I) DMSO + CCl_4 + C_6H_6, (II) DMSO + CCl_4 + $C_6H_5CH_3$ and (III) DMSO + CCl_4 + C_6H_5Cl ternary mixtures at 308.15 K

Mole fraction			ρ	u	K_s	L_f	V	Z
		x_3	(10^3 kg m^{-3})	(m s^{-1})	(10^{-10} m^2 N^{-1})	(10^{-11} m)	(10^{-5} m^3 mol^{-1})	(10^6 kg m^{-2} s^{-1})
			DMSO (1) + CCl_4 (2) + C_6H_6 (3)					
0.1004	0.1832	0.7164	1.0225	1177.7	7.0513	5.5613	8.9964	1.2042
0.1966	0.1796	0.6238	1.0330	1193.2	6.7994	5.4611	8.8779	1.2326
0.2891	0.1760	0.5350	1.0527	1200.7	6.5891	5.3759	8.6802	1.2640
0.3779	0.1725	0.4496	1.0723	1219.2	6.2738	5.2458	8.5033	1.3073
0.4633	0.1692	0.3675	1.0922	1228.9	6.0627	5.1567	8.3256	1.3422
0.5455	0.1661	0.2884	1.1153	1254.5	5.6973	4.9989	8.1317	1.3991
0.6247	0.1630	0.2123	1.1364	1274.4	5.4182	4.8749	7.9604	1.4482
0.7010	0.1600	0.1390	1.1523	1288.1	5.2304	4.7897	7.8313	1.4843
0.7746	0.1571	0.0683	1.1693	1316.5	4.9344	4.6522	7.6991	1.5394
			DMSO (1) + CCl_4 (2) + $C_6H_5CH_3$ (3)					
0.1135	0.2073	0.6792	1.0097	1154.8	7.4267	5.7074	10.2342	1.1660
0.2187	0.1996	0.5817	1.0385	1181.4	6.8992	5.5010	9.7634	1.2269
0.3164	0.1926	0.4910	1.0536	1191.2	6.6889	5.4165	9.4522	1.2550
0.4075	0.1860	0.4065	1.0733	1203.7	6.4305	5.3108	9.1221	1.2919
0.4925	0.1800	0.3275	1.0959	1239.2	5.9422	5.1052	8.7906	1.3580
0.5722	0.1741	0.2537	1.1118	1259.2	5.6726	4.9881	8.5327	1.4000
0.6469	0.1687	0.1844	1.1307	1277.9	5.4158	4.8738	8.2681	1.4449
0.7171	0.1637	0.1192	1.1509	1306.0	5.0942	4.7269	8.0104	1.5031
0.7832	0.1589	0.0579	1.1688	1322.5	4.8918	4.6321	7.7833	1.5457
			DMSO (1) + CCl_4 (2) + C_6H_5Cl (3)					
0.1102	0.2011	0.6887	1.0124	1186.9	7.0116	5.5456	11.5635	1.2016
0.2131	0.1947	0.5922	1.0348	1194.7	6.7706	5.4495	10.9444	1.2363
0.3096	0.1885	0.5019	1.0585	1205.2	6.5042	5.3412	10.3615	1.2757
0.4002	0.1828	0.4170	1.0823	1219.7	6.2108	5.2193	9.8235	1.3201
0.4855	0.1773	0.3372	1.1327	1234.8	5.7902	5.0395	9.1076	1.3987
0.5658	0.1722	0.2620	1.1688	1258.4	5.4028	4.8680	8.5717	1.4708
0.6416	0.1674	0.1910	1.1861	1279.6	5.1491	4.7523	8.2098	1.5177
0.7133	0.1628	0.1239	1.1868	1292.0	5.0477	4.7053	7.9812	1.5333
0.7812	0.1585	0.0603	1.1930	1320.6	4.8064	4.5915	7.7288	1.5755

Table 3. Values of excess isentropic compressibility (K_s^E), excess intermolecular free length (L_f^E), excess volume (V^E) and excess acoustic impedance (Z^E) of (I) DMSO + CCl_4 + C_6H_6, (II) DMSO + CCl_4 + $C_6H_5CH_3$ and (III) DMSO + CCl_4 + C_6H_5Cl ternary mixtures at 308.15 K

Mole fraction			K_s^E	L_f^E	V^E	Z^E
x_1	x_2	x_3	(10^{-10} m^2 N^{-1})	(10^{-12} m)	(10^{-6} m^3 mol^{-1})	(10^4 kg m^{-2} s^{-1})
			DMSO (1) + CCl_4 (2) + C_6H_6 (3)			
0.1004	0.1832	0.7164	-1.0635	-0.2515	-0.0082	1.0440
0.1966	0.1796	0.6238	0.5686	0.0664	0.6133	-0.9504
0.2891	0.1760	0.5350	0.2212	0.4826	0.4315	2.4498
0.3779	0.1725	0.4496	-0.1512	0.3986	0.2701	2.5708
0.4633	0.1692	0.3675	0.4106	0.6795	0.0966	3.3724
0.5455	0.1661	0.2884	-0.6705	0.2284	0.2992	1.8045
0.6247	0.1630	0.2123	-0.9829	0.0744	0.5257	0.8698
0.7010	0.1600	0.1390	-0.4730	0.2682	-0.3845	-1.0945
0.7746	0.1571	0.0683	-1.1302	-0.0980	-0.3249	0.7228

Table 3. *(Cont'd)*

Mole fraction			K_s^E	L_f^E	V^E	Z^E
x_1	x_2	x_3	(10^{-10} m^2 N^{-1})	(10^{-12} m)	(10^{-6} m^3 mol^{-1})	(10^4 kg m^{-2} s^{-1})
DMSO (1) + CCl_4 (2) + $C_6H_5CH_3$ (3)						
0.1135	0.2073	0.6792	3.5052	1.5472	0.7190	-4.2851
0.2187	0.1996	0.5817	1.4646	0.9026	0.3053	-3.3537
0.3164	0.1926	0.4910	2.3669	1.3769	0.0059	-5.3296
0.4075	0.1860	0.4065	2.5828	1.5493	-0.1059	-6.1067
0.4925	0.1800	0.3275	0.3155	0.6413	-0.4409	-3.6665
0.5722	0.1741	0.2537	0.0683	0.5445	-0.2315	-3.3768
0.6469	0.1687	0.1844	-0.2036	0.4103	-0.2613	-2.5449
0.7171	0.1637	0.1192	-1.2602	-0.1112	-0.3797	-0.1721
0.7832	0.1589	0.0579	-1.2513	-0.1674	-0.3551	0.8523
DMSO (1) + CCl_4 (2) + C_6H_5Cl (3)						
0.1102	0.2011	0.6887	7.6967	3.3105	16.8965	-18.0688
0.2131	0.1947	0.5922	7.2703	3.2591	13.8924	-17.2006
0.3096	0.1885	0.5019	6.4651	3.0289	11.0498	-15.6916
0.4002	0.1828	0.4170	5.2768	2.6112	8.4728	-13.5390
0.4855	0.1773	0.3372	2.7126	1.5661	3.9509	-7.8310
0.5658	0.1722	0.2620	0.3867	0.5612	1.0768	-2.6408
0.6416	0.1674	0.1910	-0.6901	0.0743	-0.1960	0.1383
0.7133	0.1628	0.1239	-0.3223	0.2380	-0.2644	-0.1087
0.7812	0.1585	0.0603	-1.4281	-0.3008	-0.6872	2.3919

DMSO-DMSO dipolar association releasing several DMSO dipoles. Consequently, the free dipoles of DMSO would induce moments in the neighbouring CCl_4/C_6H_6 molecules, resulting in dipole-induced dipole interactions leading to contration in volume, hence, reduction in compressibility of the system. Moreover, the possibility of weak interaction of donor-acceptor type between π-electrons of benzene ring and electronegative chlorine atom of carbon tetrachloride is always there [11]. These two effects are jointly responsible for the negative K_s^E values. In case of DMSO + CCl_4 + $C_6H_5CH_3$, toluene molecule is weakly polar (μ = 0.37 D) [23]. The presence of electron-repelling group $-CH_3$ in the benzene ring of $C_6H_5CH_3$ molecule enhances the π-electron density in the molecule, making the donation of π-electron towards electron seeking chlorine atom of CCl_4 easier, thereby accounting for increased donor-acceptor type interaction between $C_6H_5CH_3$ and CCl_4 molecules. This suggests that the interaction of carbon tetrachloride with aromatic hydrocarbons increases with the increase of $-CH_3$ groups in the aromatic ring, as pointed out by others [23]. Due to this increased interaction between CCl_4 and $C_6H_5CH_3$ molecules the dipole-induced dipole interaction between DMSO and $CCl_4/C_6H_5CH_3$ molecules seems to be slightly reduced as the mole fraction of DMSO in DMSO + CCl_4 + $C_6H_5CH_3$ system increases. Thus, a less pronounced decrease in K_s^E for DMSO + CCl_4 + $C_6H_5CH_3$ system (Table 3) than that for DMSO + CCl_4 + C_6H_6 suggests that the net attractive force between the components of the former system is less than that between the components of latter system. In case of DMSO + CCl_4 + C_6H_5Cl, chlorobenzene molecule is quite polar (μ = 1.54 D) [23]. The chlorine atom, being an electron withdrawing atom, attracts the π-electrons of the benzene ring in C_6H_5Cl molecule and thus, decreases the electron density of the ring. This makes the benzene ring a relatively poor electron donor towards the electron-seeking chlorine atom of CCl_4, thereby, a weak interaction between C_6H_5Cl and CCl_4 is expected. On the other hand, dipole-dipole interaction between DMSO and C_6H_5Cl seems to be significant and influences the variation of K_s^E with x. The over all decrease in K_s^E with x for the system DMSO + CCl_4 + C_6H_5Cl (Table 3) indicates that dipole-dipole interaction between DMSO and C_6H_5Cl molecules predominates in this system.

The values of excess intermolecular free lengths L_f^E are almost positive, and as expected, those of excess acoustic impedances Z^E are almost negative for all the three systems (Table 3). This suggests that, in addition to dipole-dipole and dipole-induced dipole interactions, dispersion forces are also operative in all these systems. It has been reported that dispersion forces tend to make a positive contribution to the excess functions [1,4] like L_f^E, while a negative contribution to Z^E is obvious.

The excess molar volumes V^E are found to be both positive and negative (Table 3) with respect to composition of the mixtures in all the systems studied. Similar variations of V^E with composition have also been reported by Kumar and Naidu [24] and Calvo *et al* [25] in some ternary liquid mixtures. For the systems I (DMSO + CCl_4 + C_6H_6) and III (DMSO + CCl_4 + C_6H_5Cl) the values change from positive to negative as the mole fraction of DMSO in these mixtures increases. It has been suggested [4,26] that K_S^L and also V^L change sign from positive to negative as the interaction between component molecules increases. This again supports our earlier view that molecular interaction between the component molecules increases with increasing amount of DMSO in these mixtures. It is evident from Table 3 that almost all the values are negative for the system II (DMSO + CCl_4 + $C_6H_5CH_3$). It may be pointed out that for the system II, the negative values of V^L may be, partly, due to the difference in the molecular sizes of the component molecules. As the molecules of DMSO (molar volume = 7.195×10^{-5} m^3 mol^{-1}) are much smaller than those of toluene molecules (molar volume = 10.767×10^{-5} m^3 mol^{-1}), which might allow the fitting of DMSO molecules into the voids created by toluene molecules, resulting in negative V^E values. A similar explanation for the negative V^E has also been proposed earlier [4,27] for the liquid mixtures.

4. Conclusion

The dependence of ultrasonic velocity on composition of the mixtures is satisfactorily represented by the eq. (1). The trends in the variations of the parameters derived from ultrasonic velocity and the sign and extent of deviation of the excess functions from rectilinear dependence on composition of these mixtures suggest the presence of molecular interaction between the components of the ternary mixtures. The interactions are primarily due to dipole-dipole and dipole-induced dipole type. Dispersion forces are also found to exist between the components of the mixtures.

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